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C-H···H-Fe Dihydrogen Bonding: Synthesis and Structure of *trans*-[FeH(NCS(*i*-Pr)-*S*)(dppe)$_2$]I (dppe=$Ph_2PCH_2CH_2PPh_2$)

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C-H···H-Fe Dihydrogen 결합: *trans*-[FeH(NCS(*i*-Pr)-*S*)(dppe)$_2$]I 착물의 합성 및 구조

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Abstract

Compound *trans*-[FeH(NCS)(dppe)$_2$] (**1**) reacted with isopropyl iodide (*i*-PrI) to give an Fe(II)-organic isothiocyanide complex, *trans*-[FeH(NCS(*i*-Pr)-*S*)(dppe)$_2$]I (**2**). Compound **2** was structurally characterized, in which the hydride ligand appears to be involved in the "dihydrogen" bonding, M-H···H-C. Crystallographic data for **2**: monoclinic space group $P2_1/n$, a=13.490(2) Å, b=17.269(3) Å, c=21.384(3) Å, β=90.682(7)°, Z=4, $R(wR_2)$=0.0348(0.0894).

요 약

화합물 *trans*-[FeH(NCS)(dppe)$_2$] (**1**)과 요오드화 이소프로필(*i*-PrI)이 반응하여 Fe(II)-organic isothiocyanide 화합물 *trans*-[FeH(NCS(*i*-Pr)-*S*)(dppe)$_2$]I (**2**)이 생성되었다. 화합물 2의 구조가 밝혀졌고, 이 화합물 내에서 hydride 리간드가 "dihydrogen" 결합에 관여한 것처럼 나타났다. 화합물 **2**의 결정학 자료: 단사정계 공간군 $P2_1/n$, a=13.490(2) Å, b=17.269(3) Å, c=21.384(3) Å, β=90.682(7)°, Z=4, $R(wR_2)$=0.0348(0.0894).

1. Introduction

Recently we reported a series of Fe(II)-H compounds of the types [Fe(H)(L)(dppe)$_2$] (L=Cl or CN) and [FeH(X)(dppe)$_2$][Y] (X=$NCCH_3$, $NCCH_2CH_2OCH_3$, $NCCH_2CH_2CH_2Cl$, NCC_6H_5, $CNCH_3$, or CNH; Y= Cl, PF_6, BF_4, or SO_3CF_3), in which dppe denotes a chelating bisphosphine ligand, bis(diphenylphosphno) ethane ($Ph_2PCH_2CH_2PPh_2$).[13] In the structurally characterized compounds of them, the Fe-H distances belong to the range of 1.311.52 Å.

As a continuation of our work on the Fe-H bond, we set out to prepare a new Fe(II)H compound of the same structural type. When compound *trans*-[FeH(NCS)(dppe)$_2$] (**1**) was treated with an organic electrophile (*i*-PrI), *trans*-[FeH(NCS(*i*-Pr)-*S*)(dppe)$_2$]I (**2**) was obtained. Compound **2** shows the so-called dihydrogen bonding, M-H···H-C, in which the hydride ligand seems to be dihydrogen-bonded simultaneously to the two C-H bonds. Here we report synthesis and structure of **2**.

2. Experimental Section

Unless otherwise stated, all the reactions have been performed with standard Schlenk line and cannula techniques under argon. Air-sensitive solids were manipulated in a glove box filled with argon.

Glassware was soaked in KOH-saturated 2-propanol for about 24 h and washed with distilled water and acetone before use, and it was either flame- or oven-dried. Diethyl ether (Et_2O) was distilled over sodium metal under argon. The NMR solvent ($CDCl_3$) was degassed by freeze-pump-thaw cycles before use and stored over molecular sieves under argon. 2-Iodopropane (*iso*-C_3H_7I or *i*-PrI) was purchased from Aldrich company. Compound *trans*-FeH(NCS)(dppe)$_2$ (**1**) was prepared by treating *trans*-[FeH(Cl)(dppe)$_2$] with KSCN.

^{1}H- and ^{13}C{^{1}H}-NMR spectra were recorded with a Varian Unity Inova 500 MHz spectrometer with reference to internal solvent resonances and reported relative to tetramethylsilane. ^{31}P-NMR spectra were also recorded with a Varian Unity Inova 500 MHz spectrometer with reference to external 85% H_3PO_4. IR spectra were recorded with a Nicolet 205 FTIR spectrophotometer. Melting points were measured with a Thomas Hoover capillary melting point apparatus without calibration. The elemental analyses were performed by the Korea Basic Science Center.

Preparation of *trans*-[FeH(NCS(*i*-Pr)-*S*)(dppe)$_2$]I, (2). Compound **1** (0.091 g, 0.10 mmol) was dissolved in 4 ml of isopropyl iodide, and the solution was stirred for 5 h. During strring, a red slurry turned to a yellow slurry. The resulting solution was filtered, and the remaining solid was washed with Et_2O (2× 10 ml) and then recrystallized from CH_2Cl_2-Et_2O to give 0.056 g (0.052 mmol, 52%) of **2**.

^{1}H-NMR ($CDCl_3$): δ 7.397-6.790 (40H, m, $Ph_2PCH_2CH_2PPh_2$), 3.165 (1H, broad, NCSC*H*$(CH_3)_2$), 2.538 (4H, broad, $Ph_2PCH_2CH_2PPh_2$), 2.110 (4H, broad, $Ph_2PCH_2CH_2PPh_2$), 1.030 (6H, broad, NCSCH$(CH_3)_2$), -19.894 (1H, quintet, $^2J_{P\text{-}H}$=48 Hz, HFe). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 135.819, 134.722, 133.575, 133.220, 130.782, 129.412, 128.603 (phenyl), 117.566 (NCSCH$(CH_3)_2$), 43.109 (NCS*C*H$(CH_3)_2$), 33.433 ($Ph_2PCH_2CH_2PPh_2$), 24.435 (NCSCH(CH_3)$_2$). ^{31}P-NMR ($CDCl_3$): δ 83.236 (d, $^2J_{P\text{-}H}$=48 Hz). mp (dec.): 178-180°C. IR (KBr): 2115 (C≡N), 1871 (Fe-H) cm^{-1}.

X-ray Structure Determination. All X-ray data were collected with use of a Siemens P4 diffractometer equipped with a Mo X-ray tube and a graphite crystal monochromator. The orientation matrix and unit cell parameters were determined by least-squares analyses of the setting angles of 70 reflections in the range 15.0<2θ<25.0°. Three check reflections were measured every 100 reflections throughout data collection and showed no significant variations in intensity. Intensity data were corrected for Lorenz and polarization effects. Decay corrections were also made. The intensity data were empirically corrected with ψ-scan data. All calculations were carried out with use of the SHELXTL programs.[4]

A yellow crystal of **2** of approximate dimensions 0.82×0.44×0.32 mm^3, shaped as a block, was used for crystal and intensity data collection. The unit cell parameters and systematic absences, *h*0*l* (*h*+*l*= 2*n*+1) and 0*k*0 (*k*=2*n*+1), unambiguously indicated

Table 1. X-ray data collection and structure refinement

formula	$C_{56}H_{56}NP_4SFeI$
fw	1081.71
temperature, K	295(2)
crystal system	monoclinic
space group	$P2_1/n$
a, Å	13.490(2)
b, Å	17.269(3)
c, Å	21.384(3)
β, deg	90.682(7)
V, Å^3	4981(1)
Z	4
d_{cal}, g cm^{-3}	1.442
μ, mm^{-1}	1.131
T_{min}	0.5371
T_{max}	0.8561
F(000)	2216
R (int)	0.0191
No. of reflections measured	9551
No. of reflections unique	9149
No. of reflections with I>2σ(I)	7702
No. of parameters refined	592
2θ range (°)	3.5-51.0
scan type	ω
scan speed	variable
GOF (goodness-of-fit on F^2)	1.020
Max., min. in Δρ (e Å^{-3})	0.941, -0.660
R	0.0348
wR_2[a]	0.0894

[a] $wR_2=\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^3 \times 10^3$)

	x	*y*	*z*	*U*(eq)[a]
Fe(1)	3143(1)	7151(1)	1725(1)	24(1)
S(1)	4600(1)	8388(1)	-5(1)	56(1)
P(1)	2148(1)	6238(1)	1329(1)	29(1)
P(2)	4306(1)	6218(1)	1673(1)	28(1)
P(3)	1938(1)	8044(1)	1877(1)	27(1)
P(4)	4101(1)	8031(1)	2238(1)	28(1)
N(1)	3563(1)	7626(1)	958(1)	31(1)
C(1)	3909(2)	7936(2)	541(1)	38(1)
C(2)	3675(3)	9025(2)	-369(2)	59(1)
C(3)	2947(4)	8566(3)	-753(2)	99(2)
C(4)	4247(4)	9592(3)	-773(2)	90(1)
C(5)	2618(2)	5307(1)	1619(1)	38(1)
C(6)	3729(2)	5258(1)	1510(1)	37(1)
C(7)	2531(2)	8986(1)	2091(1)	36(1)
C(8)	3639(2)	8974(1)	1961(1)	34(1)
C(9)	841(2)	6118(2)	1534(1)	39(1)
C(10)	82(2)	6108(2)	1088(2)	52(1)
C(11)	-894(2)	6026(2)	1268(2)	75(1)
C(12)	-1120(3)	5943(3)	1884(2)	88(1)
C(13)	-388(3)	5939(3)	2332(2)	79(1)
C(14)	605(2)	6022(2)	2155(2)	54(1)
C(15)	2120(2)	6120(2)	475(1)	37(1)
C(16)	1877(2)	6753(2)	103(1)	47(1)
C(17)	1869(3)	6688(2)	-547(1)	66(1)
C(18)	2156(3)	6011(3)	-827(2)	71(1)
C(19)	2417(3)	5387(2)	-472(2)	69(1)
C(20)	2373(2)	5429(2)	179(1)	52(1)
C(21)	5190(2)	6309(2)	1029(1)	35(1)
C(22)	6081(2)	6711(2)	1088(1)	44(1)
C(23)	6663(2)	6850(2)	571(2)	60(1)
C(24)	6379(3)	6591(2)	-11(2)	64(1)
C(25)	5515(3)	6202(2)	-76(1)	61(1)
C(26)	4910(2)	6063(2)	432(1)	49(1)
C(27)	5042(2)	5917(1)	2360(1)	35(1)
C(28)	6001(2)	5618(2)	2326(1)	46(1)
C(29)	6442(2)	5280(2)	2847(2)	60(1)
C(30)	5936(3)	5222(2)	3402(2)	59(1)
C(31)	4982(3)	5501(2)	3442(1)	56(1)
C(32)	4541(2)	5852(2)	2926(1)	45(1)
C(33)	1031(2)	7993(1)	2512(1)	32(1)
C(34)	1153(2)	7480(2)	3004(1)	41(1)
C(35)	507(2)	7489(2)	3503(1)	52(1)
C(36)	-275(2)	8003(2)	3509(1)	50(1)
C(37)	-396(2)	8525(2)	3030(1)	45(1)
C(38)	253(2)	8528(2)	2533(1)	39(1)
C(39)	1131(2)	8308(1)	1212(1)	32(1)
C(40)	1450(2)	8835(2)	768(1)	42(1)
C(41)	829(3)	9041(2)	272(1)	56(1)
C(42)	92(3)	8718(2)	210(1)	60(1)
C(43)	- 414(2)	8191(2)	636(1)	53(1)
C(44)	190(2)	7984(2)	1143(1)	40(1)
C(45)	4060(2)	8165(1)	3089(1)	33(1)
C(46)	4497(2)	8819(2)	3359(1)	42(1)
C(47)	4476(2)	8928(2)	4001(1)	51(1)
C(48)	4025(2)	8391(2)	4378(1)	55(1)
C(49)	3602(2)	7740(2)	4120(1)	52(1)
C(50)	3607(2)	7631(2)	3477(1)	38(1)
C(51)	5443(2)	8110(1)	2129(1)	34(1)
C(52)	5834(2)	8510(2)	1619(1)	45(1)
C(53)	6857(2)	8547(2)	1538(2)	59(1)
C(54)	7486(2)	8196(2)	1956(2)	64(1)
C(55)	7117(2)	7797(2)	2459(2)	58(1)
C(56)	6097(2)	7753(2)	2549(1)	45(1)
I(1)	2877(2)	10758(2)	859(2)	71(1)
I(1A)	2806(3)	10802(2)	732(5)	94(1)

[a]Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

$P2_1/n$ as a space group. The structure was solved by the direct method. All non-hydrogen atoms were refined anisotropically. The hydride ligand (Hfe) was located in the difference Fourier map and refined isotropically. All the other hydrogen atoms were generated in idealized positions and refined in a riding model.

Details on crystal data and intensity data are given in Table 1. Final atomic coordinates and some selected bond distances and bond angles are shown in Tables 2 and 3, respectively.

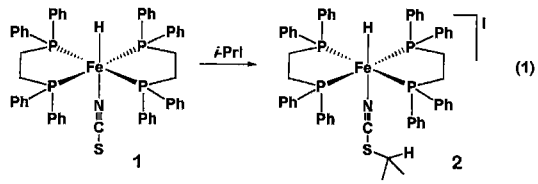
3. Results and discussion

Preparation. An Fe(II)-organic isothiocyanide complex, *trans*-[FeH(NCS(*i*-Pr)-*S*)(dppe)$_2$]I (**2**), has been prepared by the electrophilic attack of isopropyl iodide (*i*-PrI) at the isothiocyanato sulfur in a neutral Fe(II)-isothiocyanato complex, *trans*-[FeH(NCS)(dppe)$_2$] (**1**), (Eq. (1)). Stirring the isopropyl iodide solution containing **1** at room temperature gives the desired product. In this reaction, the isopropyl iodide behaves both as a reagent and as a solvent. Compound **2** is stable in the solid state, but unstable in solution.

Due to the coupling between a hydride and four equivalent phosphorus nuclei in the dppe ligands,

Table 3. Selected bond distances (Å) and bond angles (°)

Fe1-N1	1.925(2)	Fe1-P1	2.2316(7)	Fe1-P2	2.2533(7)
Fe1-P3	2.2671(7)	Fe1-P4	2.2675(7)	Fe1-Hfe	1.41(3)
S1-C1	1.693(3)	S1-C2	1.829(3)	P1-C5	1.834(3)
P2-C6	1.863(2)	P3-C7	1.865(3)	P4-C8	1.839(2)
N1-C1	1.145(3)	C2-C3	1.500(5)	C2-C4	1.523(5)
C5-C6	1.522(4)	C7-C8	1.524(3)		
N1-Fe1-P1	99.13(6)	N1-Fe1-P2	92.86(6)	P1-Fe1-P2	83.79(3)
N1-Fe1-P3	92.95(6)	P1-Fe1-P3	96.10(3)	P2-Fe1-P3	174.13(2)
N1-Fe1-P4	87.41(6)	P1-Fe1-P4	173.45(3)	P2-Fe1-P4	96.31(3)
P3-Fe1-P4	83.13(2)	N1-Fe1-Hfe	176(1)	C1-S1-C2	101.1(1)
C5-P1-Fe1	106.71(8)	C6-P2-Fe1	110.87(8)	C7-P3-Fe1	108.78(8)
C8-P4-Fe1	104.46(8)	C1-N1-Fe1	171.9(2)	N1-C1-S1	170.4(2)
C3-C2-C4	111.2(3)	C3-C2-S1	110.7(3)	C4-C2-S1	106.3(3)
C6-C5-P1	109.5(2)	C5-C6-P2	109.4(2)	C8-C7-P3	111.3(2)
C7-C8-P4	106.4(2)				



compound **2** shows a quintet for the hydride ligand in its ^{1}H-NMR spectra and a doublet for the dppe ligand in its ^{31}P-NMR spectra with a coupling constant of $J_{P\text{-}H}$=48 Hz. In addition, the Fe-H band appears at 1871 cm^{-1}.

Structure. The structure of **2** with the atomic numbering scheme is shown in Fig. 1. The coordination sphere of the Fe metal can be described as an octahedron, with the two bidentate dppe ligands at the equatorial sites and the hydride and nitrile ligands at the axial sites. The anion (I$^-$) is not bonded to the Fe metal and acts as a counter anion.

The equatorial plane, defined by the four dppe phosphorus atoms (P1-P4), is almost planar with the average atomic displacement of 0.0063 Å. The Fe metal lies 0.1219 Å above the equatorial plane. The isopropyl substituent (-CHMe$_2$) of the isothiocyanate is directed toward the open space between the two phenyl rings (C15-C20 and C21-C26), probably due to steric congestion.

The hydride ligand (Hfe) could be located and reasonably refined with an isotropic thermal parameter, and the distances of Fe-H (1.41(3) Å) appears to be somewhat reliable. The mean values of transition metalhydride (M-H) bond distances determined by neutron diffraction have been summarized by Bau and Drabnis, and the average distance of a terminal Fe-H bond is 1.575(17) Å and that of a bridging Fe-H-Fe bond is 1.664(11) Å.[5]

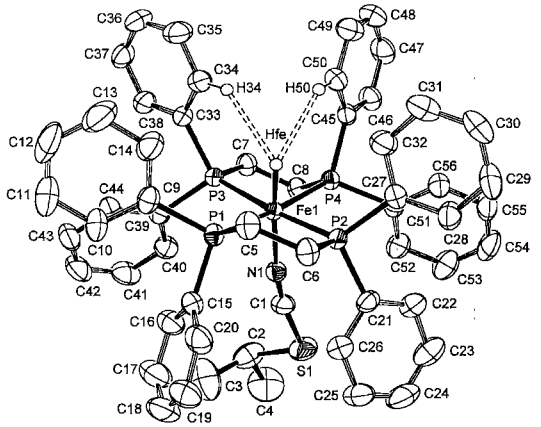
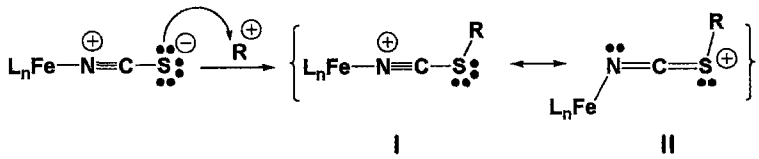


Fig. 1. ORTEP drawing of the cationic part of 2, [FeH(NCS(*i*-Pr)-*S*)(dppe)$_2$]$^+$, showing the atom-labeling scheme and 50% probability thermal ellipsoids.

The Fe-N1 bond distance (1.925(2) Å) indicates an Fe-N single bond, and the N1-C1 bond distance (1.145(3) Å) an N≡C triple bond. In addition, the bond distances of S1-C1 and S1-C2 are 1.693(3) Å



I II

and 1.829(3) Å, respectively. The Fe-N1-C1 and N1-C1-S1 bonds are linear with the bond angles of 171.9(2)° and 170.4(2)°, respectively. In addition, the C1-S1-C2 bond angle is 101.1(1)°. These bonding parameters suggest that resonance form **I** is a major contribution with the sp-hybridized nitrogen and the sp^3-hybridized sulfur atoms. In the free SCN^- ligand in KSCN, the bond distances of N≡C and C-S are 1.15(1) Å and 1.69(1) Å, respectively, and the bond angle of N-C-S is 178(1)°.[6]

Compound **2** appears to have a pseudo-C_2 axis that passes through the Fe, N1, and Hfe atoms and is perpendicular to the equatorial plane. This symmetry might reflect the equivalency of the four phosphorus nuclei in the NMR spectra of **2**. In other words, the crystal structure explains the NMR spectra that show a quintet for the H ligand in the ^{1}H-NMR and a doublet for the four P atoms in the ^{31}P-NMR spectra. The results of the X-ray structure and NMR spectral data indicate that this compound has the same structure both in solution and in the solid state.

Recently, the hydrogen bond in organometallic compounds has been the focus of research. It is now accepted that most kinds of C-H groups can act as hydrogen-bond donors.[7-13] Moreover, it has been recognized for many years that the C-H bonds can act as weak hydrogen-bond proton donors in the order: C(sp)-H>C(sp^2)-H>C(sp^3)-H.[14] Crabtree and co-workers recently proposed a new type of the "dihydrogen" bonding (M-H···H-C) in aryl phosphine (PAr_3) hydride complexes.[15] According to their own work and CSD survey, the H···H distances range from 1.50 to 2.20 Å (mean, 1.96 Å), M-H···H angles from 109 to 170° (mean, 130°) with a strong preference for the range 122-142°, and H···H-C angles from 118 to 164° (mean, 142°) with a strong preference for the range 138-148°. For comparison, the van der Waals radius of H is 1.2 Å.

Compounds **2** has the aryl phosphine (dppe) ligand, and the distances and angles of the M-H···H-C fragment, (Table 4) are highly consistent with the preferred values suggested by the Crabtree's study. On the basis of the bonding parameters described above, the hydride ligand (Hfe) appears to be involved in the dihydrogen bond of the type M-H···H-C. Moreover, this ligand seems to be dihydrogen-bonded simultaneously to the two aryl C-H bonds, which might make possible its location in the X-ray diffraction studies.

Table 4. Distances (Å) and angles (°) in the M-H···H-C fragment

H···H	Hfe···H34: 2.31
	Hfe···H50: 2.30
M-H···H	Fe1-Hfe···H34: 129
	Fe1-Hfe···H50: 130
H···H-C	Hfe···H34-C34: 135
	Hfe···H50-C50: 134

In summary, we have prepared the Fe(II)-organic isothiocyanide complex, *trans*-[FeH(NCS(*i*-Pr)-*S*)$(dppe)_2$]I (**2**), by the attack of the mild electrophile (alkyl halide, *i*-PrI) at the isothiocyanato sulfur in [FeH(NCS)$(dppe)_2$] (**2**) under mild conditions. In this reaction, isopropyl iodide behaves both as a reagent and a solvent. Molecular structure of compound **2** shows that the hydride ligand appears to be dihydrogen-bonded simultaneously to the two aryl C-H bonds.

4. Supplementary Material

Tables of full bond distances and bond angles, anisotropic thermal parameters, and atomic coordinates of hydrogen atoms are available from the author Soon W. Lee.

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